

Portable Raman Instrumentation for SERS Applications

Surface enhanced Raman spectroscopy (SERS) has attracted significant attention in recent years due to rising interest in trace level detection in the field for applications such as environmental safety, food safety, and homeland security. The worldwide number of SERS publications has jumped from approximately 3000 to 25,000 between the years 2000 and 2011[1]. The development of SERS technology is being driven by a need to overcome the technical barrier of the lower detection limit with Raman spectroscopy as well as the need for trace level detection of explosive compounds, chemical residuals, and biomedical diagnostics.

It is widely believed that surface enhancement mechanisms are mainly a result of either electromagnetic resonances between the collective oscillations of plasmons in metal particles and the incident optical field or chemical enhancement through the increase of molecule polarization after coupling with the metal surface[2]. With the advancements in nanotechnology, SERS technology has entered an era where SERS chips are made with highly controlled nanostructures on a substrate using metals such as gold or silver. Another type of SERS is solution-based that uses colloidal solutions of silver or gold particles.

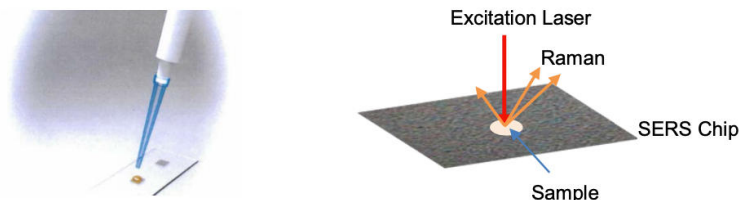


Figure 1. Illustration of a Raman Measurement Using a SERS Chip

RAMAN INSTRUMENTATION FOR SERS

For SERS developers or end users of SERS who are interested in a specific SERS application, the centerpiece of their experimental or technological platform must be a Raman setup that provides reliable lab grade performance and is affordable and portable, allowing them to tackle real world problems. The new generation of dispersive portable Raman spectrometers has brought SERS one step closer to real world applications. Due to the small area of the SERS substrate ($\sim 5 \times 5 \text{ mm}^2$) where a tiny droplet of sample solution is deposited, accurate laser focusing on the surface is an essential requirement for the Raman instrumentation. While benchtop microscopic Raman systems meet this requirement, the fact that such

instruments cannot be moved around hinders SERS developers from transferring their technologies to environments such as production lines, field testing or diagnostic locations where SERS analysis is intended to be carried out. The high cost of a benchtop micro-Raman also limits the adoption of SERS for real world applications.

The B&W Tek i-Raman Plus portable Raman system coupled with a BAC151 video microscope sampling accessory inside a BAC152 laser Class 1 enclosure is an ideal setup for SERS analysis. For solution-based SERS, if the measurement is conducted directly through the solution vial, the BCR100A Raman cuvette holder can be used with the i-Raman Plus.



i-Raman Plus



BAC151



BAC152



BCR100A

High signal to noise ratio for best limit of detection

The B&W Tek i-Raman Plus features a back-thinned CCD detector with TE-cooling to -2°C . Compared to a conventional front-illuminated CCD with a quantum efficiency at 50%, the back-thinned CCD quantum efficiency can reach up to 90%. Because of the low efficiency of the Raman phenomenon (10^{-8}), it is important that the electronic noise for the CCD detectors is at very low levels relative to the Raman signal. The TE-

cooling of the CCD device effectively reduces the noise: dark noise halves for each 7°C decrease in device temperature. The cooled detector in the i-Raman Plus allows for long integration times of up to 30 minutes. This greatly increases the detection limit and makes the low-light level applications such as SERS feasible. The 785 nm laser wavelength should be used for fluorescence reduction.

High resolution to resolve peaks of the substrate and the sample

For some SERS chips, there are intrinsic Raman peaks from the blank SERS surface. When the Raman peaks from the sample material are in the vicinity of the peaks from the blank SERS substrate, it is crucial that the sample Raman peaks can be separated from the peaks of the SERS chip. The spectral resolution for the i-Raman Plus 785S system is 4.5 cm⁻¹, which

provides adequate resolving capability to differentiate two very closely positioned peaks. **Figure 2** displays an example of two closely located peaks, with one peak (641 cm⁻¹) associated with the blank SERS and one peak (625 cm⁻¹) associated with the sample solution that is enhanced by SERS.

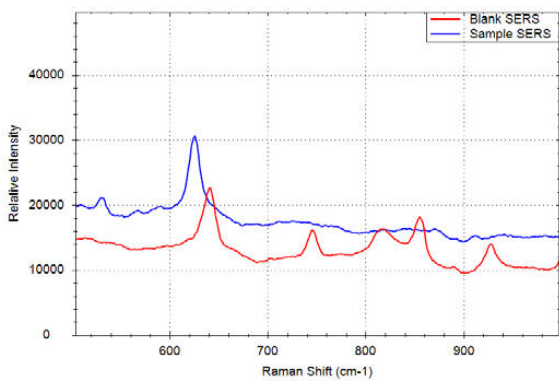


Figure 2. Raman Spectra of a blank SERS surface (red) and a sample material on SERS

Small laser beam size and accurate focusing control

Due to the fact that the SERS chips are often very small in size, small laser beam size and accurate laser focusing control are needed. The BAC151 video microscope sampling accessory coupled with the i-Raman Plus provides a laser beam size

from 21 μm up to 210 μm when objective lenses with different magnifications are used. **Table 1** displays the laser beam size and working distance when the objective lens magnification changes from 10x to 100x.

Table 1: Laser spot size from BAC151

Objective lens magnification	Working distance (mm)	Laser beam spot size (μm)
10x	16	210
20x	12	105
50x	9.15	42
100x	3.2	21

Laser safety and blocking of ambient light interference

Because many types of SERS chips will generate specular reflective light when the excitation laser beam is directed onto the SERS surface, it is necessary to have an enclosure that can shield off the reflected laser beams and at the same

time block interference from ambient light. For this, the BAC152 provides a laser Class 1 enclosure for laser safety and the necessary blocking of ambient light as well.

CONCLUSIONS

The B&W Tek i-Raman Plus portable Raman system coupled with a BAC151 video microscope sampling accessory inside a BAC152 laser Class 1 enclosure provides an ideal setup for SERS applications. The setup provides not only a high S/N ratio for best detection limit and

high resolution to resolve peaks, but also the small and adjustable laser beam size along with accurate focusing control. Last but certainly not least, the laser Class 1 enclosure provides the necessary laser safety while at the same time eliminates ambient light interference.

FURTHER READING

[Raman vs SERS... What's the Difference?](#)

REFERENCES

1. B. Sharma, R.R. Frontiera, A.I. Henry, E. Ringe, and R.P. Van Duyne, Materials Today, 2012, 15(1-2), 16-25.
2. S. Botti, S. Almariva, L. Cantarini, A. Palucci, A. Puiu and A. Rufoloni, J. Raman Spectroscopy, 2013, 44, 463–468.

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CONFIGURATION



i-Raman Plus 785S

i-Raman® Plus 785S は、弊社の革新的かつインテリジェントなスペクトロメーターテクノロジーを備えた i-Raman ホータフル型ラマンスペクトロメーターの受賞歴のあるシリーズの構成要素です。このホータフル型ラマンスペクトロメーターは、高い量子効率、TE 冷却、ならびに高いダイナミックレンジを備えた CCD アレイ検出器を用い、積分時間でさえ最長30分、低ノイズの傑出した性能を提供します。こうして、弱いラマン信号も測定することかてきます。

i-Raman Plus 785S は、 65 cm^{-1} から 3350 cm^{-1} までの測定を可能にするコンフィクレーションを有する幅広いスペクトル範囲と高分解能のユニークな組み合わせを特徴としています。システムの小さな底面、軽量構造、そして低消費電力により、とこてもラマン分析を研究レベルで実施することかてきます。i-Raman Plus には、サンプル採取を簡単にする光ファイバーフローフが装備されており、キューベットホルター、ヒテオマイクروسコーフ、フローフホルター付き XYZ スライドテーブル、ならびに弊社独自の多変量解析ソフトウェア BWIQ® および同定ソフトウェア BWID® と共に使用することかてきます。i-Raman Plus により、品質分析および定量分析のための高精度のラマンソリューションを常に使用することかてきます。



(785 nm)

ラボおよび産業用のB&W Tek社製ラマンフローフを用いた使用のためのヒテオマイクروسコーフ付きサンプル採取システム。作動距離16 mmで20倍拡大の対物レンズ付き。X、Y、およびZ軸方向の粗調整ならびに微調整、ターケティンク用同軸LED照明、サンプル観察のためのヒテオカメラが使用可能であり、標準マイクروسコーフ対物レンズと互換性があります。フローフは含まれておらず、個別にご購入いたたけます。785 nmコンフィクレーション。
BAC151C-785



直接的なレーザー放射から目および/または皮膚を保護するための、ラマンサンプル採取システム (すなわちマイクロスコフ、フローホルター) 用のカバー。ハウジングは、サンプルの装填とシステムの操作を容易にするため、人間工学に基づき設計されています。波長 532 nm、785 nm および 1064 nm における使用のため。



9.5 mm

BCR100A ラマンキューベットホルターにより、ラマンフローをホルターに固定することで液体および粉末の容易なラマンスペクトル測定ができるようになります。この付属品は、いまだかつてない再現性のために三点精密ねし付きの内蔵ミラーを使用しており、これによりラマン信号を従来のキューベットホルターの3倍まで増強します。これは、フローシャフトがキューベットに直接接触しないように設計されており、またバックグラウンド蛍光を減量するためのライトトラップも含まれています。BCR100A は、直径 9.5 mm または 12 mm のフローのため設計モデルで入手可能で、外径 12.5 mm x 12.5 mm の各標準キューベット (波長 1 cm) とともに液体や粉末のサンプル採取に用いられます。